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PLASMA-ASSISTED HETEROGENEOUS CATALYSIS FOR NOx REDUCTION IN LEAN-BURN ENGINE EXHAUST

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Abstract: Recent developments in catalytic control of NO_x are revealing the significance of NO_2 as an intermediary for achieving higher NO_x removal efficiencies. This paper discusses the combination of a plasma with a catalyst to improve the selective reduction of NO_x under lean-burn conditions. It is shown that the main effect of the plasma is to enhance the gas-phase oxidation of NO to NO_2. The reduction of NO_x to N_2 is then accomplished by the heterogeneous reaction of NO_2 with activated hydrocarbons on the catalyst surface. By using a plasma, one can take advantage of a new class of catalysts that are potentially more durable, more active, more selective and more sulfur-tolerant compared to conventional lean-NO_x catalysts. The plasma-assisted catalytic reduction process can be implemented with any type of plasma reactor and does not require a specific type of electrical power supply. It can also easily accommodate any type of catalyst support structure.

I. Introduction

The NO_x in engine exhausts is composed primarily of NO. Consequently, aftertreatment schemes have focused a great deal on the reduction of NO. Recent developments in catalytic control of NO_x are revealing the significance of NO_2 as an intermediary for achieving higher NO_x removal efficiencies.

The leading catalytic technologies for removal of NO_x from lean-burn engine exhausts are the lean-NO_x SCR catalyst [1-2] and the lean-NOx trap [3-5].

Selective catalytic reduction (SCR) is based on the reaction of NO with hydrocarbon species activated on the catalyst surface. Many studies now suggest that the conversion of NO to NO_2 is an important intermediate step in the reduction of NO_x to N_2 [6-10]. The formation of NO_2 has been found to be a necessary but not a sufficient condition for the SCR of NO.

The lean-NO_x trap involves the catalytic oxidation of NO to NO_2, followed by the formation of a nitrate on the surface. The nitrate stored on the surface is decomposed by periodically operating under rich-burn condition and so the released NO_x is reduced.

Both lean-NO_x SCR and lean-NO_x trap technologies require low sulfur fuel because catalysts that are active in converting NO to NO_2 are also active in converting SO_2 to SO_3. SO_3 leads to the formation of sulfuric acid and sulfates that increase the particulates in the exhaust and poison the active sites on the catalyst.

This paper discusses the combination of a plasma with a catalyst to improve the reduction of NO_x under lean-burn conditions. We have been investigating the effects of a plasma on the NO_x reduction activity and temperature operating window of various catalytic materials. One of our goals is to develop a fundamental understanding of the interaction between the gas-phase plasma chemistry and the heterogeneous chemistry on the catalyst surface. We have observed that plasma-

assisted heterogeneous catalysis can facilitate NO_x reduction under conditions that normally make it difficult for either the plasma or the catalyst to function by itself. By systematically varying the plasma electrode and catalyst configuration, we have been able to elucidate the process by which the plasma chemistry affects the chemical reduction of NO_x on the catalyst surface.

We have discovered that the main effect of the plasma is to induce the gas-phase oxidation of NO to NO_2. The reduction of NO_x to N_2 is then accomplished by heterogeneous reaction of NO_2 with activated hydrocarbons on the catalyst surface. The use of a plasma opens the opportunity for a new class of catalysts that are potentially more durable, more active, more selective and more sulfur-tolerant compared to conventional lean-NO_x catalysts.

II. Test Setup

Figure 1 shows one of the possible embodiments of the plasma-assisted catalyst processor. In this setup the plasma reactor is located upstream of the catalyst reactor. The same result is achieved if the catalyst is placed inside the plasma reactor.

The plasma reactor used in our study is a pulsed corona discharge reactor consisting of a metal wire inside a metal cylinder. The power supply is a magnetic pulse compression system that delivers up to 30 kV output into 100 ns pulses at repetition rates up to the kilohertz range. The catalyst structures we have investigated consisted of either a pellet bed or a monolith. Heater bands and thermocouples are used to provide active control of the plasma/catalyst processor temperature. The processor temperature can be adjusted from room temperature up to 500°C. This has been used to investigate the operating temperature window of the process.

The separate plasma/catalyst configuration shown in Figure 1 is very flexible. Although we have used a pulsed corona reactor, this type of reactor is not necessarily the only type that produces the same effect. It can be used with any type of plasma reactor and does not require a specific type of high-voltage power supply. All electrical discharge plasma reactors accomplish essentially the same gas-phase plasma chemistry for the same gas mixture [11-12].
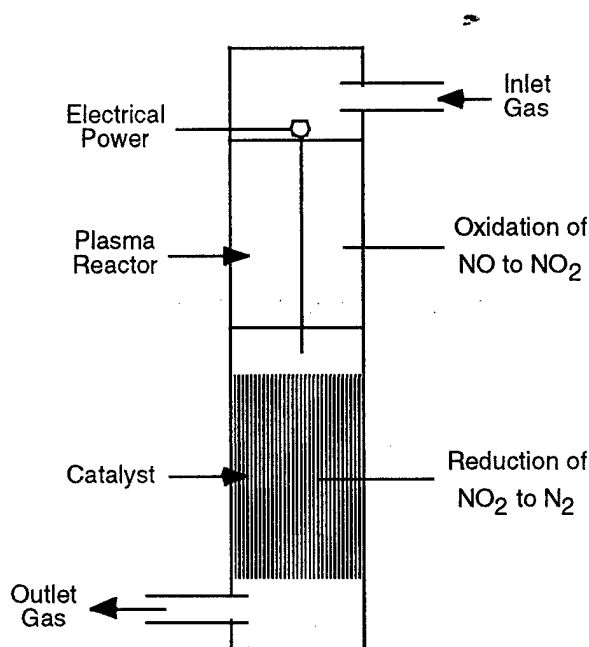

Figure 1. An embodiment of the plasma-assisted SCR process. The same result is achieved if the catalyst is placed inside the plasma reactor.

The separate plasma/catalyst configuration is also very flexible with respect to the catalyst support structure. It can be used with a bed of catalyst pellets or a monolith. For monolith structures, any L/D (length/diameter) ratio can be accommodated.
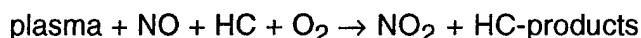
Tests of the plasma/catalyst processor have been done using both a simulated exhaust gas mixture and a real diesel engine exhaust. A gas blending manifold is used to custom make gas streams consisting of N_2, O_2, H_2O, CO_2, hydrocarbons and NO_x. These gases are metered through mass flow controllers which permitted exact control of the flow rate. After mixing in the manifold, the gas then passes through a temperature controlled heater which preheated the gas to the processor temperature. The use of custom-made gas mixtures is necessary for studying the effect of the gas composition on the gas-phase plasma chemistry and the activity of

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the catalyst. The effect of various gas components on the process products and process efficiency can thus be studied.

The plasma/catalyst processor is also connected to a generator set consisting of a Cummins B5.9 diesel engine. This enables us to test the process on a real diesel exhaust.

III. How the Process Works

The plasma-assisted catalytic reduction of NO_x is accomplished in essentially two steps. First, the plasma oxidizes NO to NO_2 in the presence of a hydrocarbon:

plasma + NO + HC + O_2 → NO_2 + HC-products

where HC refers to a hydrocarbon and HC-products refers to partially oxidized hydrocarbons. Second, the catalyst reduces NO_2 to N_2 by selective reduction using the hydrocarbons:
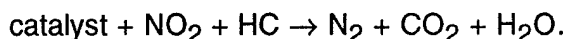
catalyst + NO_2 + HC → N_2 + CO_2 + H_2O.

Figure 2 shows the FTIR spectra of the process for a model exhaust gas consisting of 500 ppm NO, 1000 ppm (C_3) propene, 10% O_2 and balance N_2. The plasma/catalyst processor temperature is 300°C.

The spectrum of the inlet gas is shown in the top box of Figure 2. When the electrical power to the plasma reactor is turned off and this gas mixture is passed through the catalyst, the efficiencies for both the NO_x reduction and the hydrocarbon oxidation are very low, as shown in the second box ("catalyst only"). The NO_x reduction at this temperature is very low in spite of the relatively large amount of hydrocarbons available for the catalyst to do SCR.

When the electrical power to the plasma reactor is turned on, the NO is oxidized to NO_2 and the propene is partially oxidized to formaldehyde, as shown in the third box ("plasma only"). The NO_x reduction is still very low. The same amount of total NO_x (NO + NO_2) is left in the gas stream.

When the NO_2-containing gas stream from the plasma is then passed through the same catalyst,

both the NO_x and the hydrocarbons are eliminated, as shown in the bottom box ("plasma + catalyst"). This is true chemical reduction of NO_2 to N_2, and not just absorption of NO_2 on the catalyst surface. Both the original hydrocarbon and the partially oxidized hydrocarbons are eliminated in the process of reducing NO_2 to N_2.
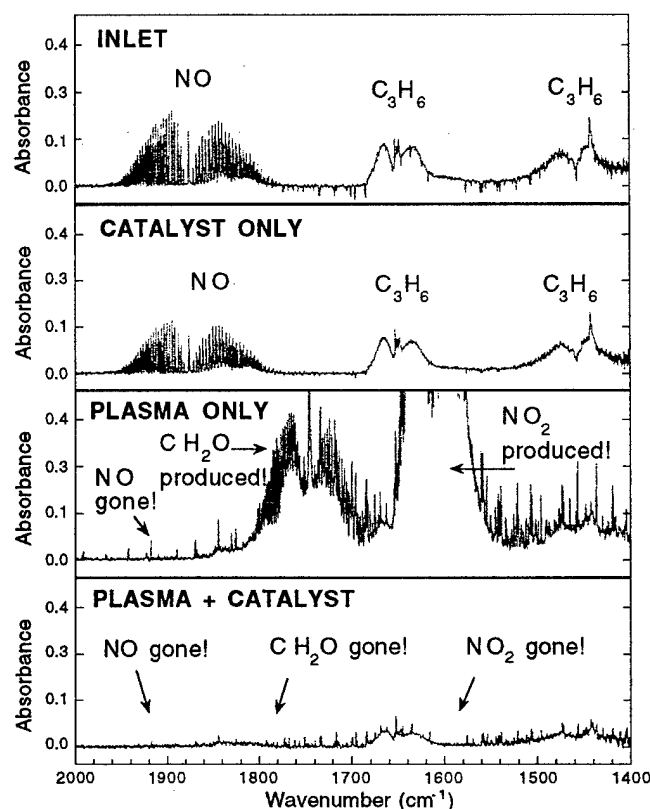

Figure 2. FTIR spectra showing the plasma-assisted catalytic reduction of NO_x.

IV. Key Features

There are three key features in the plasma-assisted catalytic reduction of NO_x.

First, the plasma oxidation process is partial. This means the plasma oxidizes NO to NO_2 but does not further oxidize NO_2 to nitric acid. The plasma also produces some partially oxygenated hydrocarbons, but does not completely oxidize the hydrocarbons to CO_2 and H_2O.

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Second, the plasma oxidation process is selective. This means the plasma oxidizes NO to NO_2, but does not oxidize SO_2 to SO_3. This makes the plasma-assisted process more tolerant to the sulfur content of fuel compared to conventional lean-NO_x technologies.

Third, by using a plasma to change the composition of NO_x from NO to NO_2, one can take advantage of a new class of catalysts that are potentially more durable and more active than conventional lean-NO_x catalysts.
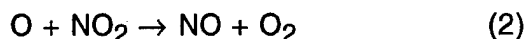
V. Role of Hydrocarbons in the Plasma

The use of a plasma does not automatically guarantee the efficient oxidation of NO to NO_2.

In exhausts containing both O_2 and H_2O, the plasma produces not only O radicals but also OH radicals. The O radical can be effective in oxidizing NO to NO_2. However, the OH radical can further oxidize NO_2 to nitric acid. This acid formation is not a desired part of the plasma process and has to be prevented.

The production of O radicals from electron-impact dissociation of O_2 has an associated cost in electrical energy. The oxidation of one NO molecule will require at least one O radical:

$$O + NO \rightarrow NO_2 \qquad (1)$$

For temperatures typical of engine exhausts, the oxidation of NO to NO_2 by the O radical becomes very inefficient. At high temperatures (for example, 300°C), the NO to NO_2 reaction is counteracted by the reduction reaction
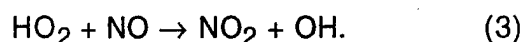
$$O + NO_2 \rightarrow NO + O_2 \qquad (2)$$

The OH radical can prevent the backconversion reaction (2), but does this at the expense of converting NO_2 to nitric acid.

The hydrocarbon plays several important roles in the plasma. The presence of the hydrocarbon prevents the formation of acid products and increases the efficiency for NO to NO_2 oxidation.

The hydrocarbon promotes the selective partial oxidation of NO to NO_2. Instead of reacting with

NO and NO_2, the O and OH radicals preferentially react with the hydrocarbons. The hydrocarbons react with O and OH to produce HO_2 and RO_2, where R is a hydrocarbon radical such as HCO and CH_3O. It is then the HO_2 and RO_2 radicals that oxidize NO to NO_2. For instance,

$$HO_2 + NO \rightarrow NO_2 + OH. \qquad (3)$$

The OH radical is reproduced when NO is oxidized by HO_2. This OH radical will in turn decompose another hydrocarbon molecule and lead to the production of more HO_2 and RO_2 radicals. The decomposition of one hydrocarbon molecule leads to the oxidation of several NO molecules. The electrical energy requirement for conversion of NO to NO_2 is therefore decreased significantly.

Because the OH radical reacts preferentially with the hydrocarbon, the oxidation of NO_2 to nitric acid is prevented. If SO_2 is present in the exhaust, scavenging of the O and OH radicals by the hydrocarbons will also prevent the oxidation of SO_2 to SO_3.

The hydrocarbon serves important roles not only on the catalyst, but also in the plasma. For lean-burn gasoline engine exhausts, the hydrocarbons are already present - mostly in the form of propene - typically at C_3 concentrations about twice that of NO. For diesel exhausts, the emitted gaseous hydrocarbon levels are much lower; however, the volatile organic fraction of the particulates could be a useful source of additional hydrocarbons.

VI. Process Products

Conventional low-temperature lean-NO_x catalysts, such as those based on Pt, can achieve NO_x reduction at the expense of producing N_2O.

Figure 3 shows the concentrations of the N_xO_y species after the plasma/catalyst processor as a function of the input electrical energy density in the plasma. Without the plasma (energy density = 0), only 20% NO_x reduction is achieved by the catalyst. This is shown by the decrease in NO

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concentration, from 500 down to 400 ppm. This NO removal is true chemical reduction of NO to N_2. Both the NO_2 and N_2O concentrations are negligible.
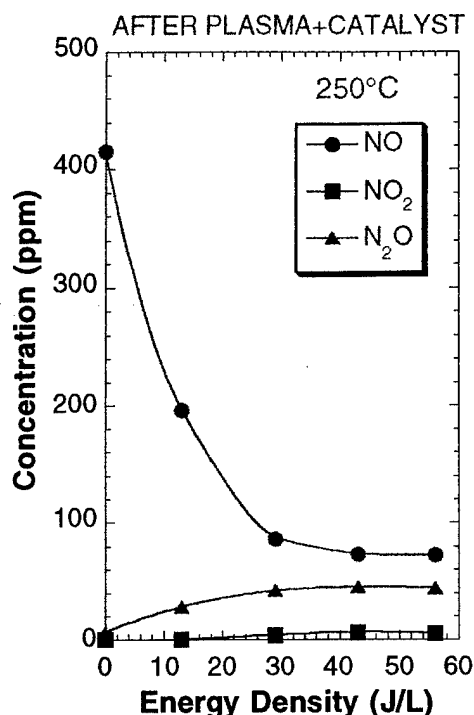

Figure 3. Plasma-assisted catalytic reduction of NO_x in a model exhaust gas at 250°C.

As the electrical energy density input to the plasma is increased, more NO is removed by conversion to NO_2. As the NO_2-containing stream goes through the catalyst, the NO_2 is reduced, mostly to N_2. As shown in Figure 3, the NO_2 concentration is very low after the plasma + catalyst. Also, only a relatively small amount of N_2O is produced at 250°C and below, even when the overall NO_x removal efficiency is high. At temperatures of 300°C and above, the formation of N_2O is negligible.

As mentioned previously, the presence of hydrocarbons prevents the formation of nitric acid and SO_3 in the plasma.

VII. Treatment of Real Diesel Exhaust

Figure 4(a) shows the efficiency for plasma oxidation of NO to NO_2, presented as a function of the electrical energy density in the plasma. Figure 4(b) shows the efficiency for reduction of NO_x to N_2, after the plasma and catalyst.
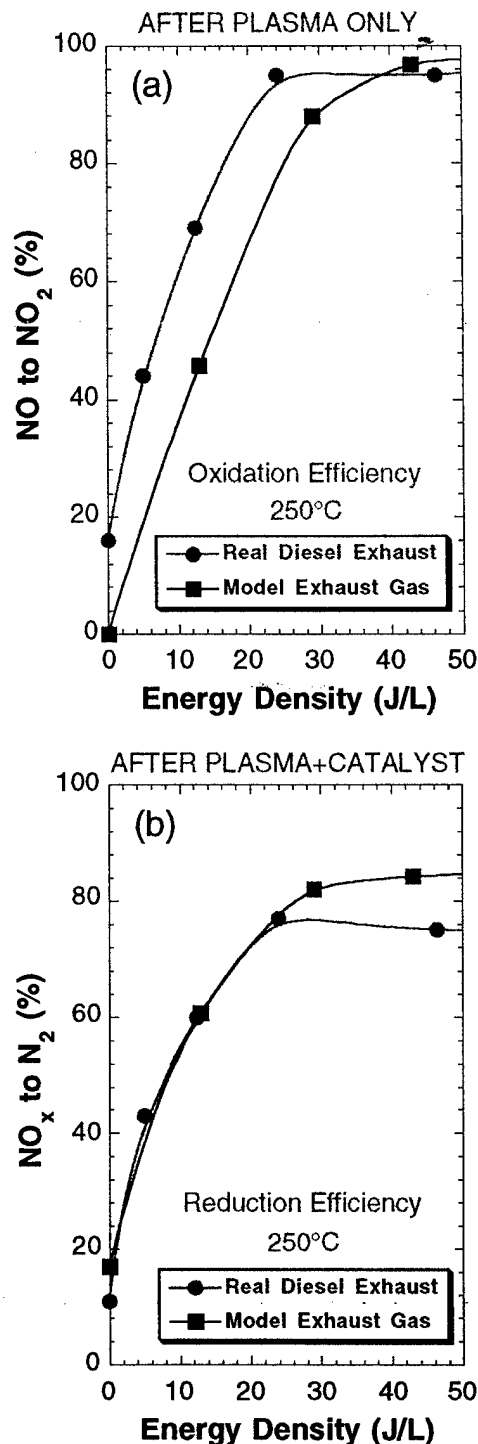

Figure 4. (a) Plasma oxidation efficiency and (b) NO_x reduction efficiency, in a real diesel exhaust compared to those in the model exhaust gas.

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The results using the exhaust from a Cummins diesel engine are compared to those taken using the model exhaust gas. The processing of the real diesel exhaust and the simulated exhaust show very similar results in both the plasma and the catalyst.

VIII. Conclusions

Plasma-assisted heterogeneous catalysis can enhance the NO_x reduction under conditions that normally make it difficult for either the plasma or the catalyst to function by itself. By systematically varying the plasma electrode and catalyst configuration, we have been able to elucidate the process by which the gas-phase plasma chemistry affects the chemical reduction of NO_x on the catalyst surface. Our results are consistent with recent studies that reveal the significance of NO_2 as an intermediary for achieving higher NO_x removal efficiencies. We have shown that the main effect of the plasma is to enhance the gas-phase oxidation of NO to NO_2. The reduction of NO_x to N_2 is then accomplished by the heterogeneous reaction of NO_2 with activated hydrocarbons on the catalyst surface. The use of a plasma opens the opportunity for a new class of catalysts that are potentially more durable, more active, more selective and more sulfur-tolerant compared to conventional lean-NO_x catalysts.

Lean-NO_x catalysts are inherently multi-functional when targeted towards NO. Recent studies have been devoted to separating the oxidative and reductive functions of the catalyst in a multi-stage system [13]. This method works fine for systems that require hydrocarbon addition; the hydrocarbon can be injected between the oxidation catalyst and the reduction catalyst. For a lean-burn exhaust that already has a significant amount of hydrocarbons, the oxidation catalyst for NO is also active for the oxidation of the hydrocarbon; this results in a decrease in the efficiency of the hydrocarbon reductant. With plasma-assisted catalysis there is no longer a need to develop catalysts that can oxidize NO to NO_2 but not oxidize the hydrocarbon reductant. This method is also more tolerant to the sulfur content of the fuel because it will not oxidize SO_2. The function of the catalyst can be greatly simplified by focusing on the reduction of NO_2. Plasma-assisted NO_x reduction can also work with both lean-NO_x SCR and lean-NO_x trap technologies.

The plasma-assisted catalytic reduction process is very flexible. It can be implemented with any type of plasma reactor and does not require a specific type of electrical power supply. This flexibility gives us the freedom to choose the least expensive and most durable plasma reactor-power supply combination. The process can also accommodate any catalyst support structure. We can choose to put a bed of catalyst pellets inside the plasma reactor, or put a catalyst monolith downstream of the plasma reactor. In the latter case, the volumes of the plasma and the catalyst can be optimized separately.

IX. Acknowledgments

X. References

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